Effect of Temperature on Adsorption Behavior and Corrosion Inhibition Performance of Imidazoline-Type Inhibitor

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ABSTRACT

In the present study, the effect of temperature on the adsorption/desorption kinetics and thermodynamics of diethylenetriamine talloil fatty acid imidazoline (DETA/TOFA imidazoline) is studied on a gold coated crystal using a quartz crystal microbalance (QCM) in a CO₂ saturated 1wt% NaCl aqueous solution. Concurrently, the corrosion inhibition performance of imidazoline on API 5L X65 steel was also investigated at different temperatures using linear polarization resistance (LPR). QCM results show that the adsorption of imidazoline-type inhibitor generally follows the Langmuir adsorption process and the desorption of inhibitor is favored with increasing temperature. While both adsorption and desorption rate constants increase with temperature, the effect on desorption was found to be more pronounced. Inhibition test results generally agree well with those obtained in the adsorption study and the loss of corrosion inhibition efficiency observed at higher temperature is attributed to a greater rate of desorption of the inhibitor.

Key words: QCM, adsorption kinetics, adsorption thermodynamics, imidazoline inhibitor, temperature effect

INTRODUCTION

As CO₂ corrosion is one of the major threats to operational safety in oil and gas production, the use of organic corrosion inhibitors to control CO₂ corrosion is of great interest to the industry. Consequently, many research projects have explored inhibition performance in various production environments.©2017 by NACE International.
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The effect of temperature on corrosion inhibition performance is a particularly significant concern. Generally, organic inhibition performance is governed by adsorption/desorption behavior. Inhibition efficiency of physisorbed inhibitors decreases with temperature, whereas for chemisorbed inhibitors inhibition efficiency usually increases with temperature\(^4\text{–}^6,9\text{–}^{11}\). However, little is known about the underlying mechanisms as, up until now, most corrosion inhibitor research has focused on inhibition efficiency, instead of on adsorption behavior itself. Use of in situ methods to study adsorption behavior of corrosion inhibitors are anticipated to lead to an improved understanding of how they function.

The quartz crystal microbalance (QCM) is a device that can measure mass changes in situ on a crystal surface at the \(\mu\text{g}\cdot\text{cm}^{-2}\) level\(^1\). Therefore, it is an ideal technique for studying temperature effects on adsorption/desorption processes. In the study reported herein, a generic corrosion inhibitor termed talloil diethylenetriamine imidazoline (TOFA/DETA imidazoline) was chosen for testing. Temperature effects on adsorption are examined by studying the adsorptive behaviors of TOFA/DETA imidazoline inhibitor at various temperatures using a QCM. In addition, the influence of temperature was investigated by studying corrosion inhibition performance at various temperatures using linear polarization resistance (LPR). As a result, temperature effects on adsorption kinetics and thermodynamics and corrosion inhibition performance were determined.

**EXPERIMENTAL PROCEDURE**

**Equipment**

**QCM Measurements**

The adsorption behavior of the chosen imidazoline-type inhibitor was studied using a Stanford Research System (SRS) quartz crystal microbalance (QCM200). The system consists of a controller, a crystal oscillator, a crystal holder, and gold-coated quartz crystals (total surface area of 4 cm\(^2\), AT-cut, 5 MHz).

![Figure 1: Setup of the QCM in a glass cell](image)

The QCM tests were carried out in a glass cell, as shown in Figure 1, with the electrolyte consisting of a 1 wt.% NaCl aqueous solution. CO\(_2\) gas was sparged continuously during the test to remove oxygen and maintain a constant CO\(_2\) partial pressure. The solution was stirred with a stir bar at a speed of 200 rpm. A temperature probe was used to monitor the temperature of the solutions during these tests. The solution pH was continuously recorded with a pH probe immersed in the electrolyte. Once the solution had been purged for more than two hours and the desired temperature had been achieved, the pH of the solution was adjusted to 4.0 by adding deoxygenated dilute HCl or NaHCO\(_3\) solution. The QCM holder was then immersed into the test electrolyte and the test was started. Experiments were carried out at various temperatures and concentrations; the test matrix is shown in Table 1.
Table 1

Test matrix for QCM tests

<table>
<thead>
<tr>
<th>Description</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test Solution</td>
<td>1 wt.% NaCl Solution, pH 4.0</td>
</tr>
<tr>
<td>Stir bar rotating speed / rpm</td>
<td>200</td>
</tr>
<tr>
<td>Total Pressure / bar</td>
<td>1</td>
</tr>
<tr>
<td>Temperature / °C</td>
<td>25, 50, 80</td>
</tr>
<tr>
<td>Inhibitor</td>
<td>TOFA/DETA imidazoline</td>
</tr>
<tr>
<td>Inhibitor Concentration / ppm</td>
<td>11, 22, 44, 88</td>
</tr>
</tbody>
</table>

Corrosion measurements

The corrosion behavior of API 5L X65 pipeline steel was investigated using electrochemical methods and surface analysis. The chemical composition of the API 5L X65 used in the present study is given in Table 2. The steel displayed a quenched and tempered microstructure.

Table 2

Chemical composition of API 5L X65 used in the experiments

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>S</th>
<th>P</th>
<th>V</th>
<th>Mo</th>
<th>Ni</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.13%</td>
<td>1.16%</td>
<td>0.26%</td>
<td>0.009%</td>
<td>0.009%</td>
<td>0.047%</td>
<td>0.16%</td>
<td>0.36%</td>
<td>Balance</td>
</tr>
</tbody>
</table>

A three-electrode glass cell was used to study the inhibition performance of the corrosion inhibitor. The working electrode (WE) was a cylindrical electrode, 1.2 cm diameter by 1.4 cm in height. A platinum mesh was used as a counter electrode (CE). In addition, an external saturated silver/silver chloride (Ag/AgCl) electrode was used as a reference electrode (RE) via a Luggin capillary. The solution was also mixed using a stir bar at 200 rpm. The setup is shown in Figure 2.

Figure 2: Configuration of a 3-electrode glass cell
The electrolyte selected in corrosion experiments was also a 1 wt.% NaCl aqueous solution. The test solution was continuously sparged with CO₂ to remove oxygen and maintain the partial pressure of CO₂ during the experiments. When the desired temperature was achieved, the pH of the solution was adjusted to 4.0 using diluted deoxygenated HCl or NaHCO₃. Before inserting the WE into the solution, it was polished with 200 grit, 400 grit and 600 grit sand paper, rinsed with alcohol and dried with N₂. In addition, 2 square specimens (1.27 x 1.27 x 0.2 cm) were used in each test for additional information. They were processed with the same procedure as WE. Those specimens were immersed in the solution at the same time when WE were immersed. During the tests, a deoxygenated and diluted HCl solution was also injected to maintain the solution pH which tended to increase, due to the ongoing corrosion process releasing corrosion products. The test matrix of corrosion measurements is given in Table 3. The corrosion rate was monitored using linear polarization resistance (LPR). Polarization resistance measurements were performed from -5 mV from the open-circuit potential (OCP) to +5 mV from OCP at a scanning rate of 0.125 mV/s. Initially, the corrosion rate before the injection of corrosion inhibitor was recorded as a baseline. Following inhibitor injection, corrosion rate was monitored until it stabilized for more than 5 hours.

**Table 3**

**Test matrix for corrosion measurements**

<table>
<thead>
<tr>
<th>Description</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature / °C</td>
<td>25, 50, 80</td>
</tr>
<tr>
<td>Inhibitor Concentration / ppm</td>
<td>22, 44, 88</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>2L 1 wt% NaCl solution saturated with CO₂</td>
</tr>
<tr>
<td>pH</td>
<td>4.0</td>
</tr>
<tr>
<td>Stirring Bar Speed / rpm</td>
<td>200</td>
</tr>
<tr>
<td>Techniques Applied</td>
<td>linear polarization resistance (LPR), open-circuit potential (OCP)</td>
</tr>
</tbody>
</table>

**RESULTS AND DISCUSSION**

**Effect of inhibitor concentration on adsorption behavior**

The rate of mass change due to adsorption measured on a gold coated substrate is shown in Figure 3 for different concentrations of inhibitor at 25°C. When there was no inhibitor present in the solution, the recorded mass change rapidly reached a steady value after inserting the QCM holder in the solution. This curve was set as the baseline. The mass change due to adsorption on the gold coated crystal with 11 ppm of the inhibitor in solution increased over 80 minutes and finally plateaued at 18.97±0.01 μg·cm⁻². Similarly, with 22 ppm inhibitor in the solution, the mass change increased for almost 40 minutes and finally stabilized at a constant value of 19.21±0.01 μg·cm⁻². For 44 ppm and 88 ppm imidazoline-type inhibitor in the solution, the mass increased with time for approximately 20 minutes and became stable at 20.14±0.01 μg·cm⁻² and 19.95±0.01 μg·cm⁻², respectively.
A significant observation in each dataset was the time required to attain a stable mass gain. It is noteworthy that with a doubling of the concentration of inhibitor added to the solution (11 ppm → 22 ppm → 44 ppm → 88 ppm), the time for reaching close to the adsorption equilibrium was approximately halved (85 min → 43 min → 25 min → 20 min). This observation indicates that adsorption rate was related to the concentration of corrosion inhibitor.

The adsorption mass change of imidazoline-type inhibitor over time at 50°C is given in Figure 4. The adsorption rate and equilibrium mass both increase with concentration, similarly to what was observed at 25°C. Adsorption mass change of imidazoline-type inhibitor over time at 80°C is given in Figure 5. Similar trends were observed at 80°C as at 25°C and 50°C.
Effect of temperature on adsorption thermodynamics and kinetics

The role of inhibitor concentration on the rate of adsorption is introduced above. In this section, the role of temperature on adsorption thermodynamics and kinetics is discussed in more details. Several adsorption models have been described for corrosion inhibitors\textsuperscript{13}. In this work, the Langmuir adsorption model was chosen as a starting point as it is the simplest. Langmuir adsorption only considers fundamental adsorption steps and neglects other factors such as interactions between molecules\textsuperscript{14}. Key aspects can be described as follows.

Forward reaction:
\[
\text{inhibitor(bulk)} \xrightarrow{\text{adsorption}} \text{inhibitor(surface)}
\]  

Forward reaction rate:
\[
\vec{r} = k_a (1 - \theta)c
\]  

Backward reaction:
\[
\text{inhibitor(surface)} \xrightarrow{\text{desorption}} \text{inhibitor(bulk)}
\]  

Backward reaction rate:
\[
\vec{r} = k_d \theta
\]  

Net reaction:
\[
\frac{d\theta}{dt} = \vec{r} - \vec{r} = k_a (1 - \theta)c - k_d \theta
\]  

Where, \( \theta \) is a parameter commonly defined as the surface coverage of corrosion inhibitor, \( k_a \) is the adsorption rate constant, \( k_d \) is the desorption rate constant and \( c \) is the inhibitor concentration.

After integration, a relationship between coverage and time can be written as:
\[
\theta(t) = K'[1 - \exp(-kt)]
\]
Where:

\[ k = k_a c + k_d, K' = \frac{c}{(c + \frac{k_a}{k_d})} \]  

(7)

The kinetic constants of the general Langmuir adsorption process can be then determined. On the other hand, when at equilibrium, the forward reaction rate equals the backward reaction rate:

\[ \hat{r} = k_a (1 - \theta)c = \hat{r} = k_d \theta \]  

(8)

In another form:

\[ \frac{k_a}{k_d} = \frac{\theta}{1-\theta}c = K_{eq} \]  

(9)

Furthermore,

\[ \Delta G_{ads} = -RT\ln K_{eq} \]  

(10)

Where, \( K_{eq} \) is equilibrium constant, and \( \Delta G_{ads} \) is adsorption Gibbs energy at standard conditions.

These general kinetics and thermodynamics information can be used to analyze the adsorption behavior. To illustrate the temperature effect on the thermodynamics of adsorption, the adsorbed inhibitor mass change at equilibrium is given in Figure 6. The adsorbed inhibitor mass is defined as the equilibrium mass adsorbed on the gold-coated quartz crystal, which can be calculated from the difference between the mass at equilibrium and the baseline mass (adsorbed mass when no inhibitor is present).

Figure 6 shows that the adsorbed mass increases with inhibitor concentration at a constant temperature. According to Equation (9), when the inhibitor concentration increases, \( K_{eq} \) does not change because \( k_a \) and \( k_d \) do not change at a fixed temperature. As a result, the coverage \( \theta \) is supposed to increase, which means that more inhibitor is adsorbed at the crystal surface at equilibrium. However, at 25°C, when the inhibitor concentration doubled from 44 ppm to 88 ppm, the adsorbed mass at equilibrium rather remained stable or only slightly decreased from 6.2 \( \mu g \cdot cm^{-2} \) to 6.0 \( \mu g \cdot cm^{-2} \). This phenomenon indicates that the crystal surface may have been already fully covered by inhibitor molecules with the 44ppm corrosion inhibitor in solution at 25°C. Therefore, even when the inhibitor concentration was doubled, the mass adsorbed did not measurably increase. In conclusion, the maximum amount of inhibitor that could be adsorbed on gold coated crystal was estimated to be at 6.2 \( \mu g \cdot cm^{-2} \). Considering this information, coverage can be defined as:

\[ \theta = \frac{m_{ads}}{m_{ads,max}} \]  

(11)

Another important observation was that a less inhibitor was adsorbed at equilibrium at increased temperature for the same concentration. This suggests that desorption was favored at higher temperature. Now that a way of quantifying coverage is defined in Equation (11), it is possible to find more information about the kinetics of adsorption using Equation (6) and Equation (7). Using the least square method, experimental data were fitted to the Langmuir kinetics. Fitting results are listed in Table 4. The \( R^2 \) in the table is the statistical measurement of how close the data are to the fitted line: a good fit is obtained when the value of \( R^2 \) is close to 1. From the table, it can be seen that in most conditions, \( R^2 \) is higher than 0.95, which means that experimental coverage vs. time curve shows good agreement with the Langmuir adsorption process. This also suggests that the adsorption of imidazoline-type inhibitor generally follows the Langmuir model. Kinetic parameters can be calculated using Equation (7)(7) from obtained \( K' \) and \( k \) values. Calculated \( k_a \) and \( k_d \) values are listed in Table 5.
Figure 6: Adsorbed mass at equilibrium at various temperatures

Table 4
Fitted results for the Langmuir adsorption process

<table>
<thead>
<tr>
<th>Temperature/°C</th>
<th>Inhibitor concentration/ppm</th>
<th>K'</th>
<th>k</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>22</td>
<td>0.9</td>
<td>2.54</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>44</td>
<td>1</td>
<td>4.61</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>88</td>
<td>0.94</td>
<td>7.50</td>
<td>0.99</td>
</tr>
<tr>
<td>50</td>
<td>22</td>
<td>0.73</td>
<td>2.45</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>44</td>
<td>0.76</td>
<td>6.07</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>88</td>
<td>0.83</td>
<td>12.31</td>
<td>0.99</td>
</tr>
<tr>
<td>80</td>
<td>22</td>
<td>0.64</td>
<td>4.82</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>44</td>
<td>0.66</td>
<td>14.37</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>88</td>
<td>0.84</td>
<td>18.27</td>
<td>0.95</td>
</tr>
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</table>

Table 5
Calculated adsorption and desorption rate constants

<table>
<thead>
<tr>
<th>Temperature/°C</th>
<th>Inhibitor concentration/ppm</th>
<th>Adsorption rate constant $k_d/10^5$mol·L⁻¹·h⁻¹</th>
<th>Desorption rate constant $k_d$/mol·L⁻¹·h⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>22</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>44</td>
<td>4.37</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>88</td>
<td>3.34</td>
<td>0.42</td>
</tr>
<tr>
<td>50</td>
<td>22</td>
<td>3.37</td>
<td>0.67</td>
</tr>
<tr>
<td></td>
<td>44</td>
<td>4.38</td>
<td>1.44</td>
</tr>
<tr>
<td></td>
<td>88</td>
<td>4.86</td>
<td>2.03</td>
</tr>
<tr>
<td>80</td>
<td>22</td>
<td>5.87</td>
<td>1.72</td>
</tr>
<tr>
<td></td>
<td>44</td>
<td>8.99</td>
<td>4.87</td>
</tr>
<tr>
<td></td>
<td>88</td>
<td>7.28</td>
<td>2.89</td>
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</table>
To better illustrate the change of adsorption parameters, the change of $k_a$ and $k_d$ with temperature is plotted in Figure 7. It is clear that both reaction rate constants increase with temperature according to the fundamental equation of reaction kinetics, which can be expressed as:

$$k_{\text{reaction}} = A \exp\left(-\frac{E}{RT}\right)$$  \hspace{1cm} (12)

where, $k_{\text{reaction}}$ is reaction rate constant, $E$ is reaction activation energy, $T$ is temperature, $R$ is the gas constant and $A$ is a pre-exponential constant. According to Equation (12), a linear relationship should be obtained between $\ln(k)$ and $1/T$ to determine the activation energies of the adsorption and desorption reactions. This relationship is shown in Figure 7, $E_a$ (adsorption reaction activation energy) and $E_d$ (desorption reaction activation energy) were calculated as 164 J·mol$^{-1}$ and 415 J·mol$^{-1}$ based on Equation (12).

![Figure 7: Relationship between lnk and 1/T](image)

Although $k_a$ and $k_d$ both increase with temperature, their dependence on temperature is not the same. As shown in Figure 8, the ratio of $\frac{k_d}{k_a}$ increases with temperature, which suggests that $k_d$ increases faster than $k_a$ with temperature leading to a reduction in surface coverage. This means that an increase of temperature favored desorption over adsorption.

![Figure 8: Temperature dependence of $\frac{k_d}{k_a}$ by QCM results](image)

Effect of inhibitor concentration on the corrosion inhibition performance

The previous section concluded that the desorption of inhibitor seemed to be favored at higher temperatures. However, one of the aims of this study is also to investigate the effect of temperature on inhibition performance, not just on adsorption/desorption behavior. Therefore, additional experiments were performed considering corroding samples at different temperatures. These could theoretically be performed using a QCM equipped with iron coated crystals. However, this technique would not be
appropriate in this study since mass gain due to inhibitor adsorption would occur simultaneously with mass loss due to corrosion. Instead, the experiments were performed in an electrochemical cell with the cylindrical X65 WE as the corroding surface.

In general, the corrosion rate started at a fairly high value and decreased quickly with time with the injection of inhibitor. It usually reached a stable steady state value within three to four hours, depending on temperature. In comparison, QCM results clearly showed a similar behavior but the steady state was achieved within only one hour. This discrepancy can be attributed to the effect of corrosion on the substrate metal which undermines the adsorption phenomenon.

At 25°C, the corrosion rate dropped from 2 to 0.12, 0.11, and 0.10 mm/y with the addition of 22 ppm, 44 ppm, and 88 ppm inhibitor, respectively (Figure 9(a)). However, at 50°C (Figure 9(b)), with 22 ppm imidazoline-type inhibitor, corrosion rate was still high (2.5 mm/y compared to a baseline of 4 mm/y). With 44 ppm and 88 ppm inhibitor, corrosion rate dropped to 0.6 and 0.4 mm/y.

It was more difficult to obtain a stable corrosion rate at 80°C (Figure 9(c)). Corrosion rate even increased to 7 mm/y with 22 ppm corrosion inhibitor. An “inhibited” corrosion rate of 2 mm/y was obtained at the end of the experiment with 44 ppm of inhibitor. Unexpected results were observed with 88 ppm corrosion inhibitor: the corrosion rate dropped to 0.2 mm/y after 24 hours but significant localized corrosion areas were observed on the corroded sample surface after examining the WE used in this experiment. To confirm the occurrence of localized corrosion, another square specimen was tested in the same conditions. Again, a large localized corrosion area was identified and characterized using a profilometer as shown in Figure 10. This localized corrosion feature had a flat bottom and covered large part of the specimen surface (6 mm long on a 12 x12 mm specimen). In addition, the depth of this attack was about 100 μm in 24 hours leading to a rate of localized corrosion of 36.5 mm/y, which was 7 to 8 times higher than the general corrosion rate (4.7 mm/y) without corrosion inhibition. Obviously, the low corrosion rate obtained with LPR was not representative of this localized corrosion. However, the localized corrosion was mitigated with a higher concentration of corrosion inhibitor. In another experiment with 176 ppm corrosion inhibitor in the solution, no localized corrosion was observed and the corrosion rate was only 0.26 mm/y after 24 hours (Figure 11).
Figure 9: Corrosion rate change vs. time before and after corrosion inhibitor injection, purple dotted line indicates when inhibitor was injected

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To summarize the results, the corrosion inhibition efficiency, which is assumed to be equivalent to inhibitor surface coverage, was calculated using:

\[
\text{Efficiency}(\theta) = \left(1 - \frac{CR_{\text{inh}}}{CR_{\text{unin}}}\right) \times 100\%.
\]  

(13)

Where \( CR_{\text{unin}} \) is the baseline corrosion rate recorded before the injection of corrosion inhibitor and the \( CR_{\text{inh}} \) is the stabilized corrosion rate at the end of each experiment.

The calculated results are given in Table 6. It can be seen that inhibition efficiency usually increases with increasing concentration of corrosion inhibitor at a constant temperature. For example, inhibition efficiency increased from 38\% \rightarrow 82\% \rightarrow 89\% with 22 ppm, 44 ppm, 88 ppm corrosion inhibitor at 50°C, respectively. In addition, inhibition efficiency decreases with temperature. Inhibition efficiency decreased from 95\% \rightarrow 82\% \rightarrow 60\% with 44 ppm corrosion inhibitor at 25°C, 50°C and 80°C, respectively. The observed pattern is similar to that obtained for the adsorption study on an inert gold substrate. This similarity confirms that coverage obtained from corrosion inhibition efficiency is closely related to adsorption behavior.
Table 6 Summarization of experimental results

<table>
<thead>
<tr>
<th>Temperature/°C</th>
<th>Inhibitor concentration/ppm</th>
<th>Initial corrosion rate</th>
<th>Final corrosion rate</th>
<th>Observed localized corrosion</th>
<th>Final inhibition efficiency</th>
</tr>
</thead>
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<td></td>
<td></td>
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<td></td>
</tr>
<tr>
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<td>22</td>
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<td>0.12</td>
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<td>93%</td>
</tr>
<tr>
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<td>44</td>
<td>1.9</td>
<td>0.11</td>
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<td>95%</td>
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<td></td>
<td>88</td>
<td>1.7</td>
<td>0.10</td>
<td>No</td>
<td>94%</td>
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<td></td>
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<td>176</td>
<td>4.2</td>
<td>0.26</td>
<td>No</td>
<td>93%</td>
</tr>
</tbody>
</table>

Effect of temperature on the adsorption thermodynamics

In the QCM part, it was shown that the adsorption of imidazoline-type inhibitor generally follows the Langmuir adsorption process. Similarly, the θ vs. time relationship obtained from corrosion inhibition experiments was also fitted with Langmuir adsorption process. In the corrosion tests, θ represents the inhibition efficiency and is calculated through Equation (13). In the QCM tests, θ was determined by the ratio of steady state adsorbed mass by maximum adsorbed mass (Equation (11)). In most cases, the θ vs. time relation showed acceptable fitting results (R²≥0.98). This again indicates, as expected, that the change of corrosion rate is directly related with the adsorption of corrosion inhibitor. The thermodynamic parameter $k_d/k_a$ was first determined using steady state inhibition efficiency via Equation (9). The obtained $k_d/k_a$ then was compared with the $k_d/k_a$ value calculated from QCM results, as shown in Figure 12. Here, cases with poor R² were not used in this comparison, including the case with localized corrosion. It was found that the obtained values from two different sets of experiments, however, are very much the same. This observation shows that evaluating the surface coverage via ratio of mass adsorbed or via corrosion efficiency yields similar outcome in term of equilibrium adsorption constants at temperature from 25°C to 80°C. This could warrant further investigation on the validity of the “surface coverage” concept commonly used to represent adsorption phenomena – this discussion is however beyond the scope of this study.

Efforts to extract kinetics constants $k_a$ and $k_d$ were comparatively much less successful. Fitting between the experimental data and Equation (6) ($θ$ vs. time relationship) showed noticeable deviation in the transient stage, i.e. first hour or so of testing (not shown). Although this behavior is not fully understood, it is thought that the competing effect of corrosion and inhibitor adsorption plays a key role.
CONCLUSIONS

- Adsorption of TOFA/DETA imidazoline inhibitor on gold generally followed the Langmuir adsorption process from 25°C to 80°C over a range of concentrations. Desorption was favored at higher temperature because the desorption rate constant $k_d$ increased faster with temperature than the adsorption reaction rate $k_a$.
- Corrosion inhibition tests on mild steel generally showed the same behavior as observed on gold coated quartz crystals. At a constant inhibitor concentration, the inhibition efficiency/equilibrium coverage decreased with increasing temperature.
- Failure in inhibition was observed at higher temperature or at low inhibitor concentration. This led to either low inhibition efficiency or localized corrosion.

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